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ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS FY 73

Ann L. Alford

Environmental Protection Agency

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ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS, FY 73

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ABSTRACT

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SECTION I

RECOMMENDATIONS

Analytical data about specific past and present pollutant sources should be used to establish and enforce effluent water quality standards for the industrial permit program and to update these standards as information is obtained. More laboratories concerned with environmental quality should be equipped to perform analyses such as those described in this report. Existing analytical techniques should be continually improved, and new techniques should be investigated for applicability to pollutant analysis. Information about specific pollution incidents should be widely disseminated to help solve and perhaps prevent future environmental problems.

SECTION II

INTRODUCTION

The National Water Contaminants Characterization Research Program (NWCCRP)* at the Southeast Environmental Research Laboratory (SERL) develops techniques for identifying and quantifying chemical pollutants and identifies specific compounds associated with various pollution sources. The NWCCRP has analyzed many samples related to a variety of specific pollution problems. Analytical results were reported only to the persons who requested the analyses and therefore had limited distribution. The problems studied by the NWCCRP are briefly summarized in annual reports[1,2] to acquaint other researchers and administrators with the type of information that can be obtained and to inform environmental chemists of technique applications and developments. This report summarizes fiscal year 1973 projects.

*In late 1973 this group's name was changed to the Analytical Chemistry Branch, but the projects described in this report were performed under the NWCCRP designation.

SECTION III

DISCUSSION

1. Terpenes in Paper Mill Effluents and Mississippi River Samples

The NWCCRP was requested by the Environmental Protection Agency's (EPA) Region VI Lower Mississippi River Field Facility in Slidell, Louisiana, to identify specific compounds in two paper mill effluents and in three river water samples. Organic pollution of the Mississippi River near New Orleans, Louisiana, was indicated by taste and odor problems in fish from the area. When six terpenes were identified in the New Orleans finished drinking water, paper mills near St. Francisville, Louisiana, were suspected as possible sources.

Three-day composite samples (1800 ml total volume each) were taken from the effluents of two paper mills, which were located approximately eight miles apart, and from three nearby Mississippi River sites (Figure 1). Each sample was extracted with chloroform, concentrated, and analyzed with gas chromatography (GC). The extracts' gas chromatograms were compared to determine which paper mill effluent components might also be present in the river water.

Each sample was then analyzed with a combined gas chromatograph-mass spectrometer (GC-MS) interfaced with a small dedicated computer. Appropriate mass spectra were plotted after the computer-reconstructed chromatograms were compared to previously obtained gas chromatograms. Specific compounds were identified by comparison of their mass spectra with standard spectra in the SERL's files or in the literature, by computer matching[3,4] with standard spectra in a data bank containing more than 11,000 spectra, or by a combination of these methods.

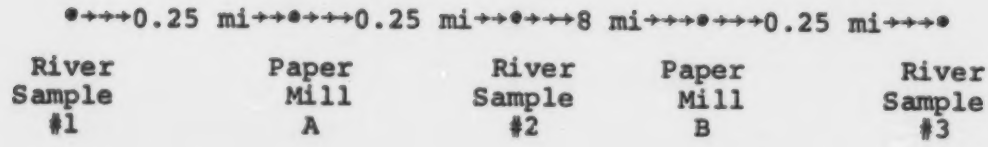

Figure 1. Diagram of sampling sites for paper mill effluent analyses

Twenty-one compounds that were absent from the solvent blank and from the sample taken upstream from both mills were identified in the two mill effluents (Table 1). Of these compounds, five identified in paper mill A effluent were also found in river sample #3. None of the six terpenes previously identified in the New Orleans finished drinking water were found in any of these samples. Absolute concentrations of identified compounds were not determined. However, low concentrations were indicated by the large concentration factor (2×10^5) required to identify river water contaminants.

Mass spectral identifications were reported to the EPA Region VI Enforcement Division Office and were compiled with other analytical data. All data were then sent to the U. S. Attorney in Dallas, Texas, who concluded that insufficient evidence existed for litigation.

2. Organic Components of Pesticide Plant Effluent

The EPA's Lower Mississippi Field Facility in Slidell, Louisiana, requested the identification of specific organic components in a pesticide plant effluent to permit development of efficient monitoring techniques.

The effluent of the pesticide manufacturing plant, located near Memphis, Tennessee, was included in industrial effluents

Table 1. ORGANIC COMPOUNDS IDENTIFIED IN PAPER MILL EFFLUENTS AND MISSISSIPPI RIVER SAMPLES

Compound	Solvent Blank (Conc. Factor $2x10^5$)	River Sample #1 (Conc. Factor $2x10^5$)	Paper Mill #1 (conc. Factor $6x10^5$)	River Sample #2 (Conc. Factor $2x10^5$)	Paper Mill #2 (Conc. Factor $6x10^5$)	River Sample #3 (Conc. Factor $2x10^5$)
bis(2-ethylhexyl)azelate	X		X			X
dichloropropene	X	X				X
1,1-diethoxypropane	X	X		X	X	X
n-nonyl aldehyde	X			X		X
3,5,5-trimethylhexanol	X					
hexachloroethane		X		X		
guaiacol		X	X	X	X	X
camphor			X	X		X
fenchyl alcohol			X	X		X
terpinene-4-ol			X	X		
α-terpineol			X	X		
β-pinene			X			
limonene			X			
fenchone			X			
anethole isomer "a"			X			
anethole isomer "b"			X			
anethole isomer "c"			X	X	X	X
2-formylthiophene				X	X	X
2-acetylthiophene				X	X	X
2-propionylthiophene				X	X	X
dimethylsulfone				X	X	
n-undecane					X	
n-dodecane					X	X
n-tridecane					X	
n-tetradecane					X	
n-pentadecane						

Table 1. (Continued)

Compound	Solvent Blank (Conc. Factor $2x10^5$)	River Sample #1 (Conc. Factor $2x10^5$)	Paper Mill #1 (Conc. Factor $6x10^5$)	River Sample #2 (Conc. Factor $2x10^5$)	Paper Mill #2 (Conc. Factor $6x10^5$)	River Sample #3 (Conc. Factor $2x10^5$)
n-hexadecane					X	
ethylidenecyclopentane					X	
methyl trisulfide					X	
norcamphor					X	
diphenylethane				X		
4-methyl-2-pentanol						X
syringaldehyde						X
						X

monitored during an EPA Mississippi River water quality survey. The plant's effluent was sampled bi-weekly for six months. Gas chromatographic analyses showed the pesticides endrin, dieldrin, aldrin, and heptachlor and other chlorinated compounds with relative retention times different from those of known pesticides.

Extracts of a solvent blank and of twelve samples of the pesticide plant's effluent were sent to the NWCCRP for GC-MS analysis. An aliquot of each extract was injected into a gas chromatograph to establish optimum separation conditions. A computer-controlled GC-MS was used to record mass spectra. As GC peaks eluted, mass spectra were collected continually and stored in the computer for later output with appropriate background spectra subtracted.

Computer matching[3,4] of effluent component mass spectra with standard spectra in a central data bank was unsuccessful in most cases. Each spectrum was inspected and compared to standard spectra in the literature. A combination of methods produced tentative identifications of 44 effluent components that were not found in the solvent blank (Table 2); 30 of these were chlorinated compounds. Many were pesticide by-products whose spectra were not included in the data bank. Few standards were available for confirmation, and many identifications were based on literature spectra of related compounds and on the analyst's knowledge of the principles of mass spectrometry.

The identifications were reported to the Administrator of Region VI for correlation with other analytical data acquired during the survey. The analyses indicated that monitoring of the plant's effluent should be continued with

Table 2. COMPOUNDS TENTATIVELY IDENTIFIED IN PESTICIDE PLANT EFFLUENT

Compound Name	Sample Number										
	1	2	3	4	5	6	7	9	10	11	12
1. Acenaphthene				X	X						
2. Aldrin					X						
3. Chlordane	X	X	X	X		X	X	X	X		X
4. Chlordene	X	X	X	X	X	X	X	X	X	X	X
5. Cymene					X						
6. Dicyclopentadiene					X						
7. Dieldrin	X				X	X	X	X			
8. Dimethylnaphthalene isomer					X						
9. Diphenylether				X		X					
10. Endrin	X			X	X	X	X				
11. Endrin isomer				X	X						
12. 1,2-Epoxy-4,5,6,7,8,8a-hexachloro-α-dicyclopentadiene (hexachlor epoxide)	X	X	X	X		X	X	X	X	X	X
13. Ethylnapthalene isomer					X						
14. Heptachlor	X	X	X	X	X	X	X	X	X	X	
15. Heptachloronorbornene isomer	X	X	X	X	X	X					
16. Heptachlornorbornene isomer		X		X	X	X	X		X	X	X
17. Hexachlorobutadiene		X		X					X		X
18. Hexachlorocyclopentadiene				X	X		X				
19. Hexachloronorbornadiene isomer	X	X	X	X	X	X	X	X	X	X	X
20. Hexachloronorbornadiene isomer		X									
21. Hexadienal											X
22. Hydroxybiphenyl isomer											X
23. Isodrin	X				X	X	X				
24. Jasmone		X		X	X		X		X		X
25. Methylnapthalene isomer					X						

Table 2. CONTINUED

Compound Name	Sample Number										
	1	2	3	4	5	6	7	9	10	11	12
26. Naphthalene					X						
27. Nonachlor				X							
28. Octachlorocyclopentene	X		X	X			X	X			
29. Pentachlorocyclopentadiene					X						
30. Pentachloronorbornadiene isomer					X						
31. Pentachloronorbornene isomer									X		
32. Pentachloronorbornadiene epoxide isomer	X										
33. Pentachloronorbornene isomer									X		
34. Phthalate ester				X							
35. Tetrachlorocyclopentene isomer							X		X		
36. Tetramethylbenzene isomer				X							
37. Trichlorocyclopentene isomer				X	X				X	X	X
38. Trichlorocyclopentene isomer									X		
39. Trichlorocyclopentene isomer		X							X		
40. Trichlorocyclopentene isomer		X									
41. Xylene					X						
42. $C_{10}H_7OCl_7$									X		X
43. $C_{12}H_9Cl_5$ (related to Endrin)					X						
44. $C_{12}H_{10}Cl_6$				X	X						

emphasis on total effluent content rather than on GC analysis for only a few specific pesticides.

3. Organic Compounds Formed During Chlorination of Municipal Waste Sludge

Intensive chlorination to disinfect sludges from sewage treatment plants and septic tanks prompted the EPA's investigation of the possibility that toxic compounds are formed during this treatment. The NWCCRP was requested by the EPA's advanced Waste Treatment Laboratory in Cincinnati, Ohio, to identify specific chlorinated compounds formed during Purifax treatment of sludge from a municipal waste treatment plant. The Purifax process, which involves mixing the sludge with large amounts of chlorine (2 g Cl_2/ℓ sludge), deodorizes and stabilizes the sludge against petrefaction for up to six months. Therefore, it must produce sludge components that are toxic to bacteria and that may be toxic to other organisms.

Two sludge samples from the Fairlawn, New Jersey, municipal waste plant, one taken before and one after Purifax treatment, were extracted to give acid, basic and neutral fractions. The acid fraction was esterified with diazomethane. Aliquots of all fractions were analyzed with gas chromatography. The Coulson conductivity GC detector showed that chlorine- and/or sulfur-containing compounds were present in all samples taken before and after Purifax treatment.

The acid fraction of the after-treatment sample contained several GC peaks not present in the before-treatment sample. This suggested that some compounds were formed during the Purifax process. GC analysis with a flame ionization

detector established the necessary conditions for combined GC-MS analysis of the additional peaks in the after-treatment sample. Mass spectral data indicated the presence of several fatty acid esters and other non-chlorinated organics. Only four minor components appeared to be chlorinated compounds. Two were specifically identified and confirmed as the methyl esters of 2,4-dichlorophenol and 2,4,6-trichlorophenol; the concentration of each was estimated to be 10 µg/ℓ. Two other chlorinated aromatic compounds were not specifically identified.

These analyses indicated the need for further investigations to determine the specific compounds synthesized during Purifax sterilization and their environmental implications. An EPA grant is currently funding such investigations at North Texas State University.[5] Information obtained will be used to evaluate Purifax chlorination and to establish guidelines for final disposition of Purifax-processed sludges and supernatant liquors.

4. Organic Components of Dye Plant Effluent

The EPA's Region IV Research and Development Program Representative requested analyses to determine if a sulfur black dye plant's wastewaters could be used as a dechlorinating agent. A Charlotte, North Carolina, dye manufacturing plant was developing (under an EPA Demonstration Grant) a treatment process for sulfur black dye wastewaters. About 25% of the plant's effluent is sodium thiosulfate, which is an excellent dechlorinating agent and is used in production of the dye Sulfur Black 1. The effluent had been proposed as a dechlorinating agent for treated sewage, but organic components of the effluent could make it undesirable for this purpose.

The NWCCRP's routine organic extraction techniques[6] were used to separate volatile organics into acid, basic, and neutral fractions. GC analysis showed no significant peaks in basic or neutral fractions; about 45 components were detected in the acid fraction after its esterification with diazomethane. Combined GC-MS analysis provided tentative identifications for 16 compounds, including 7 chlorinated benzoic acid derivatives (Table 3). Standard samples were available for only three of the identified compounds. Their presence was confirmed by comparison of GC retention times and mass spectra of effluent components to those of the standard samples. Wastewater component concentrations were estimated from GC peak height comparisons (Table 3).

Mass spectral data for six effluent components, five of the tentatively identified chlorinated benzoic acid derivatives and one unidentified component, were sent to Cornell University for computer interpretation with the Self-Training Interpretive and Retrieval System (STIRS) program.[7] If the reference file includes mass spectra of related compounds, this program provides extensive, if not complete, structural information. The STIRS system provided additional evidence for the five preliminary identifications but did not distinguish between isomers. The remaining compound was apparently a non-chlorinated aromatic and was not specifically identified.

Computer matching[3,4] of these six effluent component mass spectra to standard spectra in the Battelle reference library confirmed one identification and provided supporting evidence for another. No reliable matches were obtained for the remaining four spectra.

Table 3. ORGANIC COMPONENTS OF DYE PLANT EFFLUENT

Compound Name[a]	GC-MS Identification	Confirmation				Estimated Conc. (µg/ℓ)
		GC Retention Time of Standard	Mass Spectrum of Standard	STIRS[b] Evidence	Battelle Match	
benzoic acid	✓	✓	✓			110
p-chlorobenzoic acid	✓	✓	✓			20
2,4-dichlorobenzoic acid	✓	✓	✓	✓	Excellent	12
amino-chlorobenzoic acid isomer	✓			✓	Good	25-30
amino-chlorobenzoic acid isomer	✓			✓	No	25-30
amino-chlorobenzoic acid isomer	✓			✓	No	25-30
dichloromethoxybenzoic acid	✓			✓	No	<5
trichloromethoxybenzoic acid	✓					<5
myristic acid	✓					
pentadecanoic acid	✓					
palmitic acid	✓					
margaric acid	✓					
stearic acid	✓					
sulfur	✓					
dioctyl adipate	✓					
ethyl palmitate	✓					

[a]Acids actually identified as methyl esters

[b]STIRS—Self-Training Interpretive and Retrieval System computer program, Cornell University.

A black solid that precipitated from the acidified wastewater sample was identified as a sulfur black dye. Its solubility and color matched those of several sulfur black dyes.[8] The properties of a cotton swatch dyed with a sodium sulfide solution of the precipitate matched those of cotton dyed with sulfur black.

Identifications were reported to the requester, who will use bioassay and toxicity data for these compounds to determine if the effluent should be used as a dechlorinating agent. If this is not feasible, the data will be used by dye plant officials who must plan appropriate waste treatment.

5. Organic and Elemental Components of Coal-Gasification Pilot Plant Effluent

The U. S. Bureau of Mines requested mass spectrometric analysis of trace elements and specific organic components in effluent from a coal-gasification pilot plant. The Pittsburgh Energy Research Center designed and constructed the pilot plant to determine the feasibility of the Synthane coal gasification process. Coal is heated to expel gases from which synthetic natural gas is produced. The Synthane process requires large volumes of water, approximately 190 gal. for each ton of coal. Plant effluent component data were needed to develop disposal methods that could ultimately be used in full-scale operation.

The pilot plant effluent samples was shaken well to mix the relatively clear water with the oily scum floating on the surface. A 100-ml sample portion was extracted with 200 ml of chloroform, dried with sodium sulfate, and concentrated to approximately 25 ml.

Combined GC-MS analysis showed a mixture of five major and several minor volatile organic components (Figure 2). Computer matching[3] of seven sample mass spectra with reference spectra in the Battelle data bank provided good matches for all five major GC peaks and one minor peak (Table 4). Each match's reliability was indicated by the similarity index (SI), a number between 0 and 1 that showed how well the unknown spectrum matched the selected reference spectrum. Experience has shown that a good match produces a similarity index $\geq$ 0.5.

Spark source mass spectrometric (SSMS) analysis of duplicate 100-ml sample portions spiked with yttrium and zirconium as internal standards showed the presence of 26 elements in varying quantities (Table 5). The most significant detected element was selenium at a concentration of 360 µg/ℓ.

The importance of selenium is well documented.[9] Selenium is believed to be highly toxic to humans and produces symptoms similar to arsenic poisoning. In 1962, the U. S. Public Health Service Drinking Water Standards set the mandatory limit at 10 µg Se/ℓ. Selenium poisoning (both chronic and acute) of livestock has been associated with consumption of selenium-containing foodstuffs. Irrigation waters containing selenium at concentrations of 210-500 µg/ℓ cause toxic accumulations in plants, and waters containing over 500 µg/ℓ cannot be used for irrigation.

The NWCCRP's analytical data will be used by the Pittsburgh Energy Research Center's personnel to design pollution control facilities for Synthane coal-gasification plants. A technical progress report[10] currently in preparation will include these data.

Figure 2. Computer-reconstructed gas chromatogram of coal-gasification plant effluent extract

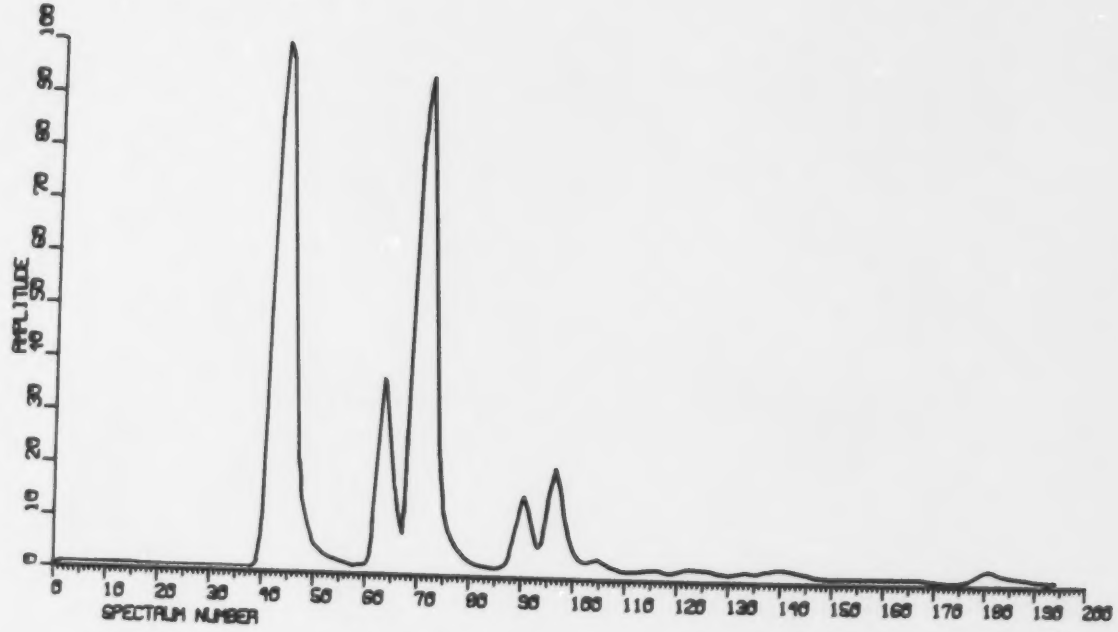

Table 4. ORGANIC COMPONENTS OF COAL-GASIFICATION PILOT PLANT EFFLUENT

RGC Peak	Best Match	S.I.	Second Best Match	S.I.
1	Phenol	0.834	Phenol	0.795
2	o-Cresol	0.846	m-Cresol	0.741
3	m-Cresol	0.867	o-Cresol	0.842
4	2,5-Dimethylphenol	0.839	2,6-Dimethylphenol	0.804
5	3,4-Dimethylphenol	0.700	3,4-Dimethylphenol	0.692
6	2,4-Dimethylphenol	0.653	3,4-Dimethylphenol	0.637
7	α-Naphthol	0.245	1,2-dihydroxy-1,2-dihydronaphthalene	0.232

Table 5. ELEMENTAL COMPOSITION OF COAL-GASIFICATION PILOT PLANT EFFLUENT

Element Detected	Concentration µg/ℓ[a]		
	Aliquot #1	Aliquot #2	Average
Si[b]	4000	5000	4500
Ca	4400	3600	4000
Na[b]	4000	2000	3000
Fe	2600	2900	2750
Mg	1500	1800	1650
S[b]	700	900	800
Al	800	700	750
Se	401	323	360
K	117	204	160
Ba	109	155	130
P	82	92	90
Zn	44	83	60
Cl[b]	48	54	50
Mn	36	38	40
Ge	32	61	40
As	44	28	30
Ni	23	34	30
Sr	33	24	30
Sn	25	26	20
Br[b]	25	20	20
Cu	16	20	20
I[b]	10	9	10
Nb	7	5	6
Cr	4	8	6
V	4	2	3
Co	1	2	2

[a]Minimum detection limit for most elements was approximately 1 µg/ℓ effluent.

[b]Concentration estimated using calculated relative sensitivity.

6. Elemental Analysis of Lake Ontario Water

The elemental components of 12 Lake Ontario water samples were determined with SSMS analysis as part of the Hazardous Materials Survey during the International Field Year for the Great Lakes (IFYGL). This joint United States-Canadian study was conducted to develop a sound scientific basis for water resource management. The sampling program involved universities, private institutions, and several United States Government agencies, including the EPA. Lake Ontario and the Ontario Basin were selected for intensive study because their physical characteristics were typical of the Great Lakes. Analytical data were needed to compile a quantitative description of hazardous materials entering, inhabiting, and leaving Lake Ontario.

The Hazardous Material Study Coordinator requested an elemental study of 12 water samples collected at three depths from four Lake Ontario sites (Figure 3). The 1-gal. samples were collected during a four-day period in late June 1972 and shipped to the SERL in glass containers. A 100-ml aliquot of each sample was evaporated onto a graphite electrode for analysis with the computerized spark source mass spectrometer, which provided quantitative data for 72 elements.

Only 24 elements were detected, and only nine were found in concentrations greater than 1 µg/ℓ (Table 6). Low signal intensities prevented quantitation of elements present at concentrations less than 1 µg/ℓ. Silicon and boron were detected in all samples, but because samples were stored in glass containers, analyses for these elements were invalid. Nitrogen, hydrogen, and oxygen were present in the vacuum system's residual gases and were therefore not determined.

Figure 3. Lake Ontario sampling sites for IFYGL elemental survey

Table 6. Elemental Composition of Lake Ontario Water Samples

	Station 10 Sample Components, µg/ℓ			Station 45 Sample Components, µg/ℓ			Station 75 Sample Components, µg/ℓ			Station 96 Sample Components, µg/ℓ		
Element	DEPTH 1m	DEPTH 60m	BOTTOM 119m	DEPTH 1m	DEPTH 90m	BOTTOM 183m	DEPTH 1m	DEPTH 120m	DEPTH 233m	DEPTH 1m	DEPTH 16m	DEPTH 35m
Ca	100	2000	3000	2000	3000	2000	2000	3000	2000	2000	2000	2000
Na	300	1000	1000	2000	2000	1000	1000	400	400	1000	1000	1000
Sr	200	200	200	100	200	100	200	100	200	200	200	200
Mg	100	200	200	300	300	200	200	300	200	200	100	400
Cl	500	300	100	200	200	100	200	200	100	200	100	300
Ba	100	100	50	100	50	100	100	100	40	40	100	<1
K	10	10	40	50	30	40	40	30	30	100	100	100
P	10	10	10	1	1	10	20	20	10	2	10	10
Al	2	4	2	1	1	1	1	1	1	2	10	1
Br	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	
As	<1		<1	<1	<1				<1	<1		
Ga			<1		<1				<1	<1		
Cr										<1		
Cu	<1		<1	<1	<1	<1	<1		<1	<1	<1	
Mn	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Fe	<1	<1	<1		<1	<1	<1	<1	<1	<1	<1	
S	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
P	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Zn			<1			<1		<1	<1			
Ni			<1		<1	<1			<1	<1		
Ba												<1
Rb					<1							
Sc					<1					<1		
Co		<1			<1		<1		<1	<1		

Mercury and inert gases were pumped away too quickly and were ignored.

Results of the elemental survey were reported to the Hazardous Materials Study Coordinator for inclusion in formal documentation of the IFYGL Study.

7. Elemental Analysis of Patio Debris

A concerned citizen's complaint to the EPA Administrator prompted the SERL's elemental analysis of floor sweepings from a patio in Tell City, Indiana. The citizen stated that air pollution was caused by black soot emissions from industrial plants in the area. His letter was accompanied by material swept from his home patio. The EPA's Office of Research and Monitoring requested the SERL to determine the sample's elemental components.

The SSMS analysis did not indicate an air pollution problem. Meaningful data acquisition was severely hampered by the sample's content of extraneous debris, leaf fragments, and brown straw components. The sample was ashed at 600° C in air for one hour and leached with boiling aqua regia. Quantitative SSMS analysis showed that silicon was the major elemental component of the soluble portion.

The SERL's report to the EPA's Office of Research and Monitoring listed quantitative data for all elements detected and stated the need for appropriate collection techniques for samples that reflect air pollution problems.

8. Elemental Analysis of Mineral Processing Plant Wastes

Spark source mass spectrometric elemental analysis provided quantitative data for the EPA's investigation of the ecological effects of taconite tailings discharged from a

Minnesota iron ore processing plant into Lake Superior. Each day the plant discharges a slurry containing approximately 60,000 long tons of taconite wastes, including 5,400 long tons of particles less than four microns in diameter. These small particles remain suspended in water and are transported by water currents. Evidence of taconite-related materials has been found in the municipal water systems of Beaver Bay, Two Harbors, and Duluth, Minnesota. Elemental analyses were requested by the EPA's National Water Quality Laboratory (NWQL) in Duluth.

The NWQL prepared a composite of the plant's discharge by combining smaller samples taken hourly for ten days. Particles larger than five microns in diameter were filtered from the composite sample, and aliquots were used for various ecological studies. One 6-ml aliquot was shipped to the SERL for elemental analysis by SSMS. The slurry was centrifuged to separate liquid and sediment. Two 1-ml liquid samples were spiked with the internal standard yttrium and evaporated onto graphite electrodes. Four sediment samples were dried and spiked with yttrium and indium for internal standards.

The SSMS method provided quantitative data for 12 elements in the liquid portion and for 28 elements in the sediment portion (Table 7). Concentrations were estimated for four other elements detected in both liquid and sediment (Table 7). Electronic detection provided an absolute sensitivity of about 0.1 µg for most elements.

At another time, the EPA's National Coastal Pollution Research Program in Corvallis, Oregon, requested the SERL to analyze for mercury and arsenic in waste tailings from the iron ore processing plant in Minnesota. Neutron

Table 7. ELEMENTS DETECTED IN ORE PROCESSING PLANT WASTE SLURRY

Element	Sediment Portion	Liquid Portion
	Concentration µg/g	Concentration µg/mℓ
Si	100,000[a]	4[a]
Fe	98,000	7
Mg	30,000	20
Ca	18,000	10
Na	7,000[a]	0.5[a]
Mn	6,000	0.3
K	3,000	9
Al	3,000	7
P	2,000	16
S	300[a]	2[a]
Cl	200[a]	0.5[a]
Sr	45	0.2
Ba	40	
Ti	14	
Zn	11	0.5
Zr	8	
Ce	6	
Y	5	
Co	5	0.1
Er	3	
Nd	3	
Sc	3	
La	2	
Sm	2	
Cu	2	0.6
V	2	
Pb	1	0.6
Nb	1	
Rb	1	
As	1	
Pr	1	
Cs	0.5	

[a]Concentrations estimated with calculated relative sensitivity.

activation analysis was used to provide an estimate of the quantities of these elements being dumped into Lake Superior. Mercury concentrations did not vary significantly in 47 samples of ore and tailings samples. In most samples, the mercury content was close to the detection limit of 10 ng/g and in no case greater than typical U. S. Geological Survey values for sediments and rocks in that area. Arsenic values, which varied from 10 to 30 µg/g, were well above the detection limit but were not uncharacteristic of natural sediments.

These data were reported to the National Coastal Pollution Research Program for compilation with other analytical data. The EPA's investigation of the ecological effects of the ore processing plant's effluent has not been completed.

9. Dissemination of Analytical Information

The NWCCRP's analytical expertise was utilized by scientists in industry, universities, and state and federal agencies. Requests were answered for publication reprints, standard samples, analytical methods and monitoring procedures, and information about previously identified wastewater components.

a. Consultations

Several requests concerned polychlorinated biphenyls (PCB's).

- A publication[11] and several oral presentations about identification and quantitation of PCB isomers in Aroclors documented the NWCCRP's knowledge and prompted more than 40 requests for samples of individual isomers and analytical information.

- A compilation of tentative EPA methods[12] included

the NWCCRP's procedure[11] as the chosen PCB-quantitation method for samples containing mixtures of more than one Aroclor.

- The author of a book on PCB's was granted permission to include melting points and infrared spectra of individual isomers synthesized at the SERL.

- Instructions for quantitative analysis of PCB's in chicken tissue were given to the South Carolina Board of Health.

- Two sewage sludge extracts were quantitatively analyzed for PCB's by the SERL method as requested by the Midwest Research Institute of Kansas City, Missouri.

- South Dakota State University personnel requested and obtained information for application of the SERL PCB method to the analyses of several hundred samples of wild birds.

- The Amarillo, Texas Municipal Water Authority received assistance with evaluation of the impact of low concentrations of PCB's in sediments and waters of streams feeding their reservoir.

The EPA's Region IV Surveillance and Analysis Division was provided immediate information about monitoring and clean-up procedures after 1400 gallons of transformer fluid containing Aroclor 1254 were spilled near Kingston, Tennessee. The immediate environmental problems were magnified by heavy rains that spread the PCB's over several acres. The contaminated area included a farm well, a dairy cattle watering pond, and a large recreational lake's draining area. Public concern demanded immediate action. Federal, state, and local resources were utilized for clean-up and

restoration of the contaminated site. The transformer manufacturer removed 11,531 drums of contaminated soil at a cost of more than $300,000 and monitored the area for several months to assure that no further water supply contamination had occurred.

The NWCCRP's knowledge of specific components of paper mill and domestic wastewaters helped to determine the sources of pollution incidents. The Montana State Board of Health requested this information to locate the cause of foam downstream from a paper mill. In Denver, Colorado, the EPA's Region VIII Surveillance and Analysis Division suspected a paper mill holding pond as the source of private well contamination. The NWCCRP provided standard samples of suspected pollutants and detailed information about sample extraction, concentration, GC analysis, and probable components.

b. Industrial Organic Pollutant List

At the request of the EPA's Effluent Guidelines Division, the NWCCRP compiled a list of organic compounds identified by combined GC-MS in industrial effluents. A list was needed to compare specific identified pollutants with compounds in reports from consultants chosen by the EPA to recommend effluent guidelines.

The list contained 257 compounds (from 22 industries) that were identified by the NWCCRP and the Region IV Surveillance and Analysis Division. The difference in compounds detected for plants within the same industries indicated that each plant is unique. Concentration, toxicity, taste, and odor information were included when available.

The report was distributed to various EPA officials for

planning research in pollutant identification, treatment, and control and was included in an EPA Research Report.[6] An expanded and updated list will be prepared periodically and will include data obtained at other EPA laboratories.

c. Symposia

During FY 73 two symposia were sponsored by the SERL and coordinated by NWCCRP personnel. In November 1972 the two-day symposium on Applications of Mass Spectrometry to Environmental Problems, which was sponsored jointly by the EPA and the University of Georgia Chemistry Department, dealt with the present and potential applications of mass spectrometry to the identification and measurement of environmental pollutants, both organic and inorganic. The twelve invited speakers presented a wide range of ideas and experiences to the 242 symposium registrants from government, university, and industrial laboratories.

The Third Symposium on Recent Advances in the Analytical Chemistry of Pollutants was held on May 14-16, 1973, in Athens, Georgia. The SERL and the University of Georgia were host sponsors. Other sponsors were the Chemical Institute of Canada, the National Research Council of Canada, and the American Chemical Society. The symposium's purpose was to bring together applied environmental analytical chemists and experts in advanced techniques with environmental applications. The 268 registrants represented diverse analytical interests and were evenly distributed from industry or research institutes, academic institutions, and government facilities.

SECTION V

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SECTION VI

GLOSSARY OF ABBREVIATIONS

EPA - Environmental Protection Agency

GC - gas chromatography

GC-MS - combined gas chromatography and mass spectrometry

IFYGL - International Field Year for the Great Lakes

MS - mass spectrometry

NWCCRP - National Water Contaminants Characterization Research Program at the Southeast Environmental Research Laboratory

NWQL - National Water Quality Laboratory

PCB's - polychlorinated biphenyls

RGC - computer-reconstructed gas chromatogram

SERL - Southeast Environmental Research Laboratory

SI - similarity index (for comparison of organic mass spectra)

SSMS - spark source mass spectrometric analysis

STIRS - Self-Training Interpretive and Retrieval System (for organic mass spectrometry)